This paper is part of the following report:

TITLE: International Conference on Electromagnetics of Complex Media
[8th], Held in Lisbon, Portugal on 27-29 September 2000. Bianisotropics
2000

To order the complete compilation report, use: ADA398724

The component part is provided here to allow users access to individually authored sections
of proceedings, annals, symposia, etc. However, the component should be considered within
the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP011588 thru ADP011680

Chiroptical Spectroscopy of Turbid Media

A. A. Kokhanovsky

Institute of Physics
70 Skarina Avenue, Minsk 220072, Belarus
Fax: 375-172-840879, E-mail: alex@zege.bas-net.by

Abstract

The influence of the size of particles on the circular dichroism (CD) and optical rotatory dispersion (ORD) spectra of turbid layers with spherical globules of chiral substances is studied. Simple equations for the values of CD and ORD of dispersed slabs with optically soft large spheres are obtained and analyzed. Equations derived can be used for the solution of the inverse problem, namely for deriving intrinsic spectra of substances inside small particles from measurements of spectra for turbid layers.

1. Introduction

Circular dichroism (CD) and optical rotatory dispersion (ORD) spectra are fingerprints of molecular asymmetries of chiral substances [1,2]. They have already been studied both for homogeneous [2] and particulate [3-8] media. It was found, in particular, that both ORD and CD spectra of turbid layers with Rayleigh-Gans particles coincide with correspondent spectra of chiral molecules in solutions. This is not the case for Rayleigh particles, where a multiplier $\dfrac{\overline{m}^2 + 2}{3}$ ($\overline{m} = \dfrac{m_L + m_R}{2}$), $m_L = n_L + i\chi_L$ and $m_R = n_R + i\chi_R$ are the relative refractive indices for left-handed and right-handed circularly polarized beams) should be used to relate the intrinsic spectra of substances to the spectra measured for turbid layers.

One should expect even more profound distortion of spectra in the case of large ($x \gg 1$, $x = ka$, $k = \dfrac{2\pi}{\lambda}$, a is the radius of particles, λ is the wavelength of the incident wave) chiral particles. The task of this paper is to relate intrinsic CD and ORD spectra of substances inside large particles to spectra measured for dispersed layers. It is assumed that the refractive index of a host medium is close to the refractive index of particles, which is usually the case for bio-liquids. It should be pointed out that the refractive index of a surrounding medium could be always adjusted to satisfy the criteria of the optical softness: $|\overline{m} - 1| \ll 1$.

2. Large Optically Soft Chiral Spheres

For the sake of simplicity we will consider turbid layers with spherical optically active particles. Also we combine ORD $\varphi(\lambda)$ and CD $\theta(\lambda)$ spectra in one complex function:

$$\Psi(\lambda) = \varphi(\lambda) + i\theta(\lambda).$$ (1)

This function can be found with the following equation in the case of turbid layers with chiral spheres [3,4]:

$$\Psi(\lambda) = \frac{2\pi N}{k^2} \int_0^\infty S(\lambda, a) f(a) da,$$ (2)

where N is the number concentration of particles, $f(a)$ is the particle size distribution and

$$S(\lambda, a) = \sum_{l=1}^\infty (2l+1) c_l.$$ (3)

Amplitude coefficients c_l are complex functions of the refractive index and size of particles [3,4]. These coefficients rapidly decrease at $l > M$, where $M \approx x$. Functions $S(\lambda, a)$ depend on the intrinsic ORD $\varphi_0(\lambda)$ and CD $\theta_0(\lambda)$ spectra of chiral substances bounded in small particles. Thus, Eqs. (1)-(3) can be used for the derivation of intrinsic spectra $\varphi_0(\lambda)$ and $\theta_0(\lambda)$ from measurements of the complex function $\Psi(\lambda)$, provided that the information on the particle size distribution and concentration of particles N is available.

The solution of the inverse problem is simplified for optically soft ($|\overline{m} - 1| \ll 1$) large ($x \gg 1$) particles, where simple expressions for the amplitude function $S(\lambda, a)$ can be obtained. Let us show it.

It follows for the amplitude coefficients of large soft spherical particles in the framework of the van de Hulst approximation [4]:

$$c_l = \frac{1}{2} x \sin \tau \Delta m \exp(i\rho \sin \tau),$$ (4)

where

$$\rho = 2x(\overline{m} - 1), \tau = \arccos\left(\frac{l + \frac{1}{2}}{x}\right), \Delta m = m_L - m_R.$$

The value of ρ is called the phase shift. Eq. (4) allows to evaluate series (3) for the amplitude function $S(\lambda, a)$ analytically. Namely, replacing the sum in Eq. (3) by integral [4]: $\sum_{l=1}^\infty \rightarrow \int_0^x dl$, where $l + \frac{1}{2} = x \cos \tau$ and $dl = -x \sin \tau d\tau$, one obtains:

$$S(\lambda, a) = x^3 \Delta m \int_0^1 \sigma^2 \exp(i\rho\sigma) d\sigma$$

or

$$S(\lambda, a) = \frac{x^3 \Delta m}{3} H(\rho),$$ (5)

where the complex function $H(\rho) = v(\rho) + iw(\rho)$ has the following simple form:

$$H(\rho) = -\frac{6i(1-e^{i\rho})}{\rho^3} + \frac{6e^{i\rho}}{\rho^2} - \frac{3ie^{i\rho}}{\rho}. \tag{6}$$

The expansion of the function $H(\rho)$ as $\rho \to 0$ for monodispersed spheres is given by:

$$H(\rho) = 1 - \frac{3}{10}\rho^2 + \frac{1}{56}\rho^4 + i\left(\frac{3}{4}\rho - \frac{1}{12}\rho^3 + \frac{1}{320}\rho^5\right) + o(\rho^6). \tag{7}$$

It follows from Eqs. (2), (5):

$$\Psi(\lambda) = \overline{H}(\rho)\Psi_0(\lambda), \tag{8}$$

where

$$\overline{H}(\rho) = \frac{\int_0^\infty H(\rho)f(\rho)\rho^3 d\rho}{\int_0^\infty f(\rho)\rho^3 d\rho},$$

$$\Psi_0(\lambda) = \varphi_0(\lambda) + i\theta_0(\lambda), \quad \varphi_0(\lambda) = \frac{\pi c \Delta n(\lambda)}{\lambda},$$

$$\theta_0(\lambda) = \frac{\pi c \Delta\chi(\lambda)}{\lambda}, \Delta n(\lambda) = n_L - n_R, \Delta\chi(\lambda) = \chi_L - \chi_R$$

and c is the volumetric concentration of a chiral substance in a turbid layer.

Eq. (8) is the main result of this paper. It follows from Eq. (8) that

$$\Psi_0(\lambda) = \overline{H}^{-1}(\rho)\Psi(\lambda). \tag{9}$$

Thus, the solution of the inverse problem is greatly simplified. It follows at small values of the phase shift (see Eq.(7)): $H(\rho) \to 1$ and $\Psi(\lambda) \to \Psi_0(\lambda)$ as it should be in the framework of the Born approximation [8].

Eq. (8) can be used for studies of the dependence of spectra $\Psi(\lambda)$ on the size of chiral particles. Spectra $\Psi_0(\lambda)$ depend on the substance in question. They can be measured or found from quantum mechanical calculations.

3. Conclusion

Turbid bio-liquids and other light scattering chiral media can be characterized by their ORD and CD spectra. It was shown here how to relate ORD and CD spectra of disperse media with intrinsic spectra of particles using simple approximate equations. This could be of importance for monitoring bio-particles during their life cycles.

The case of large soft spherical particles was studied in detail. However, results can be easily generalized on the more important and practically relevant case of nonspherical particles. The diameter of a spherical particle should be changed to the maximal length of an incident beam inside of a nonspherical particle to approximately account for the effects of nonsphericity. The account for inhomogenity and internal structure of particles is also straightforward in the framework of the approximation proposed.

References

[1] L. Pasteur, Ann. Chemie Phys., vol. 28, p. 56, 1850.

[2] P. Crabbe, *Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry.* Holden-Day, San-Francisco, 1965.

[3] C. F. Bohren and D. Huffman, *Light Scattering and Absorption by Small Particles.* Wiley, New York, 1983.

[4] A. A. Kokhanovsky, *Light Scattering Media Optics: Problems and Solutions.* Wiley-Praxis, Chichester, 1999.

[5] D. W. Urry, T. A. Hinners, and L. Masotti, *Arch. Biochem. Biophys.*, no. 137, p. 214, 1970.

[6] D. J. Gordon, *Biochemistry*, no. 11, p. 413, 1972.

[7] *Selected Papers on Natural Optical Activity*, SPIE Milestone Series, v. MS15, A. Lakhtakia (Ed.). SPIE Optical Engineering Press, Bellingham, 1990.

[8] C. F. Bohren, *J. Theor. Biology*, no. 65, p. 755, 1977.